

DETERMINATION OF TOTAL PYRIDINES AND TOTAL QUINOLINES IN IOW TEMPERATURE COAL-TAR DISTILLATES BY ULTRAVIOLET SPECTROPHOTOMETRY

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ABSTRACT

An ultraviolet spectrophotometric method for determining total pyridines and total quinolines in coal-tar distillates is described. The bases are extracted from the sample with 10% sulfuric acid. The pH of the acid extract is adjusted to 12 by adding potassium hydroxide. The free bases are extracted from the alkaline solution with isocotane, and the ultraviolet spectrum is obtained from the isocotane solution. The total quinolines and total pyridines are determined from the spectrum by using the following average absorptivities from 10 quinolines and 13 pyridines: 15.95 for quinolines at 316.5 m/m and 23.24 and 21.25 for quinolines and pyridines at 260 m/m. This method needs only a small amount of sample and can be applied to similar materials, such as petroleum distillates.

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Pyridine bases as derived from coal tar are complex mixtures of pyridine, quinoline and their homologs (5,7). For the analysis of these bases according to chemical type, (that is, as pyridines and quinolines), it was desired to develop an ultraviolet spectrophotometric method that would apply to low temperature coaltar distillates and crude tar bases.

Previously LeRosen and Wiley (6) had attempted to determine pyridines in petroleum products by extracting the sample with phosphoric acid wherein the pyridines were determined by ultraviolet spectrophotometry and expressed as pyridine by referring to a standard graph of pyridine itself. Another paper (4) described a similar process.

In the method described in this paper, pyridine and alkyl derivatives are estimated as "total pyridines," not as pyridine itself, as done by LeRosen and Wiley. Similarly, quinoline and its alkyl derivatives are estimated as "total quinolines." Briefly, the procedure is as follows: The sample is extracted with 10% sulfuric acid and the acid layer is adjusted to pH 12 by adding potassium hydroxide. The tar bases in the alkaline solution are then extracted with isocctane. The total pyridines and total quinolines are determined by the composite spectrum of the isocctane extract.

The selected wave length for calculating total quinolines is $316.5 \text{ m}\mu$, at which pyridines show no absorbance. The empirical absorptivity for total quinolines at this wave length is 15.95, the average coefficient of 10 quinolines chosen for this study. The wave length selected for total pyridines is $260 \text{ m}\mu$, at which quinolines show considerable absorbance. Their absorbance can be calculated from their concentration, as determined by the absorbance at $316.5 \text{ m}\mu$, and a correction applied to total absorbance from which pyridines may be calculated. The empirical absorptivity for total quinolines at $260 \text{ m}\mu$ is taken as 23.24, the average of 10 quinolines; that for total pyridines is taken as 21.25, the average coefficient of 13 pyridines.

APPARATUS

Beckman DK-2 Spectrophotometer with hydrogen discharge lamp. Matched pair 1-cm. silica cells. Separatory funnels. Pipettes and volumetric flasks.

CHEMICALS

Pyridine bases:
Pyridine, Fisher certified reagent.
2-Methylpyridine, C. P. Eimer and Amend.

3-Methylpyridine, 98%, Eastman Kodak Co., yellow label. 4-Methylpyridine, Eastman Kodak Co., white label. 2,3-Dimethylpyridine, Matheson, Coleman and Bell. 2,4-Dimethylpyridine, 95%, Eastman Kodak Co., yellow label. 2,6-Dimethylpyridine, 90%, Eastman Kodak Co., yellow label. 3,5-Dimethylpyridine, pure grade, Aldrich Chemical Co. 2-Ethylpyridine, 95% purity minimum, Reilly Tar & Chemical Corp. 4-Ethylpyridine, 95% purity minimum, Reilly Tar & Chemical Corp. 5-Ethyl-2-methylpyridine, Eastman Kodak Co., white label. 3-Ethyl-4-methylpyridine, pure grade, Aldrich Chemical Co. 2,4,6-Trimethylpyridine, Eastman Kodak Co., white label. Quinoline, synthetic, Eastman Kodak Co., white label. 2-Methylquinoline, Quinaldine 95%, Eastman Kodak Co., yellow label. 4-Methylquinoline, Lepidine, Eastman Kodak Co., yellow label. 6-Methylquinoline, Eastman Kodak Co., white label. 7-Methylquinoline, pure grade, Aldrich Chemical Co. 8-Methylquinoline, Eastman Kodak Co., white label. 2,4-Dimethylquinoline, pure grade, Aldrich Chemical Co. 2,6-Dimethylquinoline, Eastman Kodak Co., white label. Isoquinoline, Eastman Kodak Co., white label. 3-Methylisoquinoline, Eastman Kodak Co., yellow label. Acridine, pure grade, Aldrich Chemical Co. Sulfuric acid, 10%, analytical reagent. Sodium hydroxide, 10%, analytical reagent. Potassium hydroxide pellets, analytical reagent. Isooctane (2,2,4-trimethylpentane), spectro-grade.

EXPERIMENTAL

Procedure for Synthetic Mixtures. The ultraviolet spectra of the 23 bases used for this study were determined individually in isocotane. The spectra agreed well with those in the literature (1,3). The absorptivities of the bases and their averages at 260 m/m and 316.5 m/m were then calculated and are presented in Table I.

Stocks of synthetic mixtures containing bases listed in Table II were prepared in 10% sulfuric acid solution. Their concentrations were exactly three times those shown in the table.

The stocks to which neutral oil was added were washed three times with isooctane, which was discarded. The volume of isooctane used each time equaled that of the stock. Ten ml. of the acid layer was adjusted to pH 12 by slowly adding KOH pellets. The alkaline solution was then extracted three times with 10 ml. of isooctane. The extracts were combined, and the ultraviolet spectrum of the 30-ml. extract was determined. The concentrations of total quinolines and total pyridines were determined by the absorbances and average absorptivities at 316.5 m/m and 260 m/m, respectively.

Table III shows the recovery of bases by this method. In this table, the "present" concentrations were one-third of their stocks and the "found" were the concentrations of the 30-ml. isocotane extract of the corresponding mixtures. For example, synthetic mixture number 1 in Tables II and III has a total pyridine concentration of 0.0202 g/l. to correspond to the dilution of the original stock from 10 to 30 ml. The concentration found, as shown in Table III, was 0.0201 g/l.

<u>Procedure for Tar-Base Samples</u>. (a) For tar distillate: For samples containing 1-2% base by weight, 10 ml. of distillate was weighed in a separatory funnel and extracted three times with 10% sulfuric acid, 20 ml. the first time and 10 ml. each the second and the third times. The acid layers were collected in a 100-ml. volumetric flask. The oil residue remaining in the funnel was extracted three times with 10 ml. of 10% sodium hydroxide each time. This extraction removes any tar acids

Table I Absorptivities of Pyridine Bases

•		Length
	منز 260 m	316.5 mm
Pyridine Bases		
Pyridine	17.44	O
2-Methylpyridine	25.43	0
3-Methylpyridine	23.47	0
4-Methylpyridine	14.22	,4 . O
2,3-Dimethylpyridine	26.86	0
2,4-Dimethylpyridine	22.41	0
2,6-Dimethylpyridine	26.74	0
3,5-Dimethylpyridine	22.87	0
2-Ethylpyridine	24.47	0
4-Ethylpyridine	13.07	. 0
5-Ethyl-2-methylpyridine	20.99	. 0
3-Ethyl-4-methylpyridine	18.87	0
2,4,6-Trimethylpyridine	20.33	. <u>. 0</u>
Average	21.25	0
Quinoline Bases		
Quinoline	24.23	9.84
2-Methylquinoline	23.90	24.71
4-Methylquinoline	27.69	8.97
6-Methylquinoline	17.79	12.39
7-Methylquinoline	19.16	18.95
8-Methylquinoline	12.56	12.87
2,4-Dimethylquinoline	24.24	17.25
2,6-Dimethylquinoline	21.25	13.56
Isoquinoline	28.67	27.27
3-Methyl-isoquinoline	27.08	<u> 13.69</u>
Average	23.24	15.95

Table III Recovery of Total Pyridines and Quinolines from Synthetic Mixtures by Using Average Absorptivities2

Mixture	Totai Pyridines Present, g/1.	Total Pyridines Found, g/l.	Recovery, Percent	Total Quinolines Present, g/l.	Total Quinolines Found, g/l.	Recovery, Percent
1 2 3 4 5 6 7 8 9	0.0202 0.0282 0.0081 0.0181 0.0179 0.0179 0.01875 0.01875	0.0201 0.0281 0.0080 0.0181 0.0173 0.0192 0.0193 0.0206 0.0208	99.3 99.7 99.8 100.0 96.2 107.0 103.0 109.8 111.0	0.0155 0.0093 0.0248 0.0171 0.0184 0.01238 0.01238 0.01238	0.0155 0.0091 0.0245 0.0166 0.0201 0.0206 0.0116 0.0117	100.0 97.8 98.7 97.3 109.0 112.0 93.7 94.5
10b/ 11 12b/	0.01875 0.02203 0.02203	0.0199 0.01905 0.01868	106.0 87.0 85.0	0.01238 -0.01354 0.01354	0.0119 0.0135 0.0135	96.1 99.0 99.0

a/ At 316.5 m/m, a for quinolines = 15.95; at 260 m/m, a for quinolines = 23.24; at

²⁶⁰ m/, a for pyridines = 21.25.

b/ These mixtures contained 0.03 g/l. neutral oil obtained from low temperature tary their acid solutions (pH = 2) were extracted with isooctane to remove the neutral oil.

Table II. Composition of Synthetic Mixtures

						Atxtu	. No.					
	4	7	4	7	4	68 7	1	88	2	104	77	12ª
Total Base, 8/1.	0.03565	0.0375	0,03286	0.03519	0.0363	0.0363	0.03113	0.03113	0.03113	0.03113	0.03557	0.03557
Pyridino 2-Methylpyridine	0.00155	0.00217	0.00062	7000			0.0016	0.0016	0.0016	0.0016		
3-Mothylpyridine	0.00 0.00 55 0.00 55	0.00217	0.00062	70000	9900.0	9900*0	0.00002	0.00002	0.00202	0.0000	0.00705	0,00705
2,3-Dimothylpyridine	0.00E55	0.00217	0,00062	0.007	1		0,00284	0,00284	0.00284	0.00284		•
2,4-Dimothylpyridine	0.00155	0.00217	0.0062	1000		0.00	8 00.0	0.000.0	0.00199	0.00199		
3.5-Dimethylpyridine	0.0dl55	0.00217	0,00062	0.001	/							
2-Ethylpyridine	0.00155	0.00217	0.00062	7000								
5-Ethyl-2-mothylpyridine		0.0017	0,00062	1000			0.00204	0.00204	0.00204	0.00204	91800*0	0.00816
3-Ethyl-4-acthylpyridine		0.00217	0,00062	0.0014	0,0042	0.0042	0.00131	0.00131	0.00131	0.00131		
2,4,6-Trimothylpyridine		0.0021	0,00062	1000	8	2	0.00 C	0.0017 17.100.0	0.0 C. 00.0	0.00171	0,00682	0.00682
Total Pyridines, g/l.	0.02015	0.0282	0.00800	0.01814	0. CE 7.9	0.0179	0.01875	0.01875	0.01B75	0.01875	0.02203	0.02203
Quinoline	0,00155	0.00093	0,00248	0.00105			0.00327	0.00327	0.00327	0.00327		-
2-Methylquinoline	0.00155	0.00093	0,00248	0.001705								
4-Astry Iquinolina 6-Methylminolina		0000	0.002/8	0.001705			0.0024.2	0.00272	0.0024.2	0.00262	0.007	0.00%
7-Methylquinoline	0.00155	0.00	0.00248	0.0d 705								
8-Methylquinoline	0,00155	0,00093	0,00248	0.001705	0,00432	0.00432	0.00135	0.00135	0.00135	0,00135		
2,4-Dimethylquinoline	0,00155	0,000	0,00248	0.0g705	0,00518	0.00518	0,00162	0.00162	0,00162	0.00162 0.0000	0.0038	C COSB
Isoquinoline	9	0,000	97700	0.0 0.0 0.0 0.0 0.0 0.0	0,00582	0.00582	0.000.82	0.000 82	0,000 0 0,000 0,000 0,000 0,000 0,000 0,000 0,000 0,000 0 0,000 0 0,000	0,00182	10000	•
3-Methyl-isoquinoline	0.00155	0.00093	0.00248	0.001705	0.00308	0.00308	76000 0	0.00094	0,00094	0.00094		
Total Quinolines, g/l.	0.a55	0.0093	0,024.8	0.01705	0.0184	0.0184	0.01238	0.01238	0.01238	0.01238	0.0354	0.0354
Total Pyridines in Base Hixture, Wt. S	56.52	75.2	24.53	51.55	49.3	49.3	60.2	60.2	60.2	60.2	62.0	62.0
Total Quinolines in Base												
Mature, Mt. 8	43.48	8. 7.	75.47	18.45	50.7	50.7	39.8	39.8	39.8	39.8	38.0	38.0

I Those mixtures contained 0.03 g/l. neutral oil from low-temperature coal tar.

that may make complete extraction of tar bases difficult. The alkaline layer was discarded, and the oil layer was then extracted again three times with 10% sulfuric acid as before. These acid extracts were added to the 100-ml. volumetric flask, and the final volume of the acid solution was diluted to 100 ml. with 10% sulfuric acid.

(b) For crude tar base: About 0.1 gram of crude tar base was weighed and dissolved in 10% sulfuric acid in a 50-ml. volumetric flask. The solution was diluted to the mark with 10% sulfuric acid.

Twenty-five ml. of either of the above acid solutions was washed three times with iscoctane. The volume of iscoctane used each time equaled that of the acid solution. After washing, the volume of the acid solution was adjusted to 25 ml. with water if necessary. Two ml. of the acid solution was pipetted into a small beaker that contained a few milliliters of water and placed in an ice-water bath. Potassium hydroxide pellets were added to the acid solution with constant stirring until the pH of the solution reached 12. The solution was transferred quantitatively to a 25-ml. volumetric flask and was diluted to the mark with distilled water. Five ml. of the alkaline solution was extracted three times with 10 ml. of isooctane each time. The isoctane extracts were combined, and an ultraviolet spectrum was determined.

Calculation of Tar Bases in Sample. Average absorptivity for quinolines at 316.5 m μ = 15.95 Average absorptivity for quinolines at 260 m μ Average absorptivity for pyridines at 260 m/

$$Q = \frac{A_{316.5}}{15.95} \times F_1 \times F_2 \tag{1}$$

$$P = \frac{A_{260} - \left(\begin{array}{c} A_{316.5} \\ 15.95 \end{array} \times 23.24 \right)}{21.25} \times F_1 \times F_2$$
 (2)

where Q = total quinolines in grams, P = total pyridines in grams,

 $A_{316.5}$ = absorbance at 316.5 m μ ,

A260 = absorbance at 260 m μ , F_1 = dilution factor for final isocotane extract, if any, F_2 = dilution factor for the sample.

In the procedure described above, there is no further dilution for the final isocotane extract. Therefore, F_1 equals 1. F_2 is equal to $(30/1000 \times 25/5 \times 100/2) = 7.5$ for the distillate and $(30/1000 \times 25/5 \times 50/2) = 3.75$ for the crude tar base.

If the tar-base content in the sample is too high, further dilution of the final isooctane extract is necessary to obtain a satisfactory spectrum with absorbances at 316.5 and 260 m μ within a range of 0.1 - 0.9. The dilution factor F_1 , therefore, has to be found by the actual dilution made.

 $_{ au}$ If the tar-base content in the sample is so low that the composite spectrum of the final 30 ml. of isooctane extract is unsatisfactory, either of the following two procedures can be used: (a) Increase the volume of alkaline solution for final isooctane extraction from 5 to 10 ml. In this case, F_1 is still 1, and F_2 is changed to 3.75 instead of 7.5; (b) increase the volume of isooctane-washed

acid extract from 2 ml. to any desired volume up to 20 ml. In this case, the dilution factor F_2 has to be changed to a value depending on the actual volume of the acid solution used.

From the weight of total pyridines, total quinolines, and weight or volume of the sample used, the percentage of total pyridines and total quinolines can be calculated.

DISCUSSION

Selection of Wave Lengths and Absorptivities for Calculating Total Pyridines and Total Quinclines. The pyridine bases of tar distillates contain a great number of pyridine and quincline derivatives, and the exact composition varies with the type of tar and manner of distillation. To represent all possible compositions an unlimited number of synthetic mixtures would be required. For this study, the best one can do is to make a synthetic mixture containing the main bases found in tar distillates (5,7) as representatives. Thirteen pyridines and ten quinclines have been selected. However, several other important alkyl pyridines and quinclines, such as tetramethylpyridines and trimethylquinclines, were not included in this work because of their unavailability in this laboratory when this work was done. It is expected that these bases will not appreciably change the pattern of the composite spectrum and also that their absorptivities will not be far from the average values of the 23 bases.

Table II shows the compositions of the synthetic mixtures. The spectra of six typical synthetic mixtures, as shown in Figures 1 to 4, follow a general pattern that also applies to the spectra of pyridine bases extracted from two tar distillates (Fig. 5).

To select suitable wave lengths for calculating total pyridines and total quinolines, several key wave lengths (256, 260, 265, and 270 mp for pyridines and 304.5, 308, 313, 316.5, and 318 for quinolines) were tried. Best recoveries for the bases in the above synthetic mixtures have been found at wave lengths of 260 mp and 316.5 mp, respectively, for pyridines and quinolines. The recovery at these wave lengths is shown in Table III. For the first four mixtures, which contained all of the available pyridines and quinolines, recoveries were within 0.7%, or better, for total pyridines, and 2.7%, or better, for total quinolines. Based on the recovery and the assumption that the reference mixture of equal amounts of individual bases better represents the tar bases in the samples than other mixtures would, the following average absorptivities were chosen for calculating the total pyridines and the total quinolines in tar distillates: 21.25 for total pyridines and 23.24 for total quinolines at wave length 260 mp, and 15.95 for total quinolines at wave length 316.5 mp.

As the average absorptivity is based on the presence of many bases, the chances of its failing to be applicable will increase as the number of bases decreases. For example, if only 4-ethylpyridine with an absorptivity of 13.07 is present, the error incurred by using the average value of 21.25 will be the greatest. Likewise, the error in the quinoline determination increases as the number of quinolines in the sample decreases. However, coal-tar bases are complex mixtures, and this situation will be unlikely to happen; also, in most instances the true absorptivities of the base mixtures are expected to fall in the neighborhood of the average values.

Of the two types of bases, it is noted that the recovery for quinolines is better than that for pyridines. This is due to the fact that pyridines do not interfere with quinolines at 316.5 m μ , while quinolines interfere with pyridines at 260 m μ .

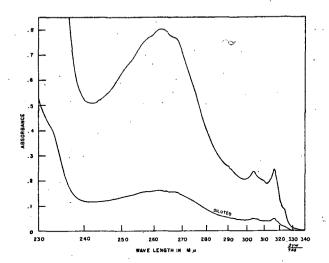


Figure 1. Spectrum of synthetic mixture 1.

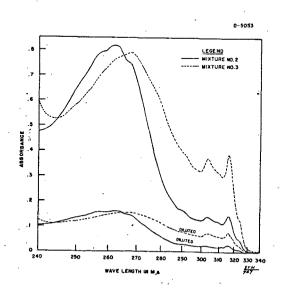


Figure 2. Spectra of synthetic mixtures 2 and 3.

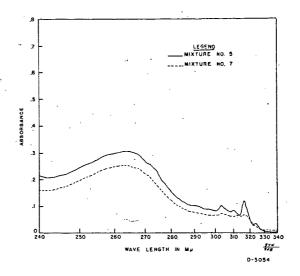


Figure 3. Spectra of synthetic mixtures 5 and 7.

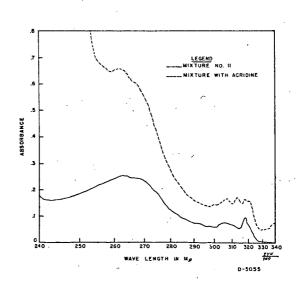


Figure 4. Spectra of synthetic mixture 11 and mixture containing acridine.

Figure 5. Spectra of base mixtures from two tar distillates

WAVE LENGTH IN M.

260

290

300 310

320 330 340

To obtain a good composite spectrum, the best concentration of the bases in isocctane is 0.03 - 0.04 gram per liter. However, this method can also be satisfactorily applied to a final isocctane extract containing a total base content as low as 0.015 gram per liter, if the quinoline content roughly equals that of the pyridines.

Interference. In extracting the bases from the distillate, a small amount of acid-soluble phenols and hydrocarbons that also possess an absorption for ultraviolet energy at 250 to 260 mp is carried over to the acid solution and eventually will interfere with the determination of the bases. However, this interference can be overcome by washing the acid extract with isocctane and by holding all phenols in the alkaline solution during the final extraction of the bases with isocctane. Synthetic mixtures 6, 8, 10, and 12, which were contaminated purposely with hydrocarbons from tar distillate, demonstrate the fairly good removal of the hydrocarbons by treating the acid extract with isocctane.

Although the tar bases in distillates consist mainly of pyridines and quinolines, they also may contain some other nitrogenous compounds, such as pyrroles, indoles and anilines (5,7). However, pyrroles and indoles are very weak bases. Their pK_b values are so close to 14 that they are not extractable with dilute mineral acids. Anilines are basic in property and are extractable with dilute mineral acids. Some of the aniline derivatives, such as toluidines, have been identified in tar bases. By examining their ultraviolet spectra (1,3), it was shown that the highest absorbance appears from 235-250 m/m while the lowest is from 260-270 m/m. Fortunately, their presence usually is in a small percentage in comparison with pyridine bases (7). In this method, the interference of this small amount of anilines can be assumed to be negligible insofar as the composite spectrum of the tar bases follows the general pattern of the synthetic mixtures. On the other hand, if the composite spectrum shows an unusual pattern with a peak at 240 to 250 m/m, it might indicate that the tar base might contain a rather higher amount of anilines than usual. Should this happen, the small amount of anilines is included as pyridines at 260 m/m, although the interference is not considered to be appreciable.

The two composite spectra (Fig. 5) of two tar distillates (Table IV) followed the general pattern of those of the synthetic mixtures. One of these distillates was obtained from a low temperature Wyoming lignite tar and the other from a low temperature bituminous coal tar. The spectrum of tar bases from the bituminous coal tar shows a small additional peak at 252 mm. This might be due to an unusually high amount of aniline derivatives or an unusually high percentage of a certain alkyl pyridine. For example, 3-ethyl-4-methylpyridine present in a comparatively larger amount than other pyridines would give a small individual peak at around 250 mm. A crude tar base, consisting of a mixture of neutral oil, tar bases, and small amounts of benzene and tar acids, was recovered as a by-product in the liquid-liquid countercurrent extraction of tar acids from the bituminous coal tar distillate using aqueous methanol (8). This crude tar base upon analysis was found to contain 70 weight-percent of total pyridines and 30 weight-percent of total quinolines. The proportion of total pyridines to total quinolines is quite similar to that for the base obtained directly from the distillate.

Analysis of Distillates Containing Acridine. High-boiling tar distillates may contain some acridines. Acridine, qualitatively and quantitatively, can be measured by a similar procedure. Its ultraviolet spectrum shows a significant peak at 339 mm which is suitable for its quantitative analysis and also shows an unusuall high absorbance at around 250 mm which can be used as a confirmation for this compound.

A synthetic mixture, which contained six pyridines, three quinolines and acridine was analyzed in the same manner as the other synthetic mixtures. The composite spectrum of the mixture and the recovery of the bases by this method are shown in Figure 4 and Table V. The absorptivity for acridine at 339 m/ is 42.2, at 316.5 m/, 13.9, and at 260 m/, 17.2

Table IV

Determination of Total Pyridines and Total
Quinolines in Tar Distillates

	Distillate		
•	Lignite	Bituminous	
	Tar	Coal Tar	
Distillation Endpoint, oc.	125.0	125.0	
Pressure, mm. Hg	0.1	0.1	
Volume of Sample Used, ml.	10.0	10.0	
Weight of the Sample, g.	9.35	9.55	
Total Pyridines Found, g.	0.103	0.104	
Total Quinolines Found, g.	0.012	0.05	
Total Base, g.	0.115	0.154	
Total Pyridines in Base, wt. %	89.5	67.5	
Total Quinolines in Base, wt. %	10.5	32.5	
Total Base in Sample, wt. %	1.23	1.62	
Total Pyridines in Sample, wt. %	1.1	1.1	
Total Quinclines in Sample, wt. %	0.13	0.52	

Table V

Recovery of Bases from a Synthetic Mixture
Containing Acridine

<u>Bases</u>	Present, gram/liter	Found, gram/liter	Recovery percent
Total Pyridines	0.0184	0.020	109.0
Total Quinolines	0.00989	0.0081	82.0
Acridine	0.0017	0.00175	103.0

Other Applications. This method can also be applied to tar refinery streams, such as the extract and raffinate, from the countercurrent liquid-liquid extraction of tar distillates with aqueous methanol and hexane (8). The bases in the hexane phase can be analyzed by this procedure directly, and the bases in the methanol phase can be purified by distillation and extraction as described elsewhere (2).

Pyridine bases present in samples from petroleum refining can also be determined by this method.

CONCLUSION

An ultraviolet spectrophotometric method developed to determine total pyridines and total quinolines in their mixtures has been shown to give satisfactory analysis of these two types of bases in coal-tar distillates. This method should work equally well for the bases in similar materials.

LITERATURE CITED

- (1) American Petroleum Institute Research Project 44, "Catalog of Ultraviolet Spectral Data."
- (2) Chang, Ta-Chuang Lo, Karr, Clarence, Jr., manuscript in preparation.
 (3) Friedel, R. A., Orchin, Milton, "Ultraviolet Spectra of Aromatic Compounds,"
 John Wiley and Sons, Inc., New York, 1951.
 (4) Hofmann, Edward, Arch. Hyg. u. Bakt. 128, 169-78 (1942).
 (5) Kruber, von, O., Racithel, A., Grigoleit, G., Erdől und Kohle 8, 637-43 (1955).
 (6) LeRosen, H. D., Wiley, J. T., Anal. Chem. 21, 1175-77 (1949).
 (7) Lowry, H. H., "Chemistry of Coal Utilization," pp 467-73, John Wiley and Sons, Inc., New York, 1947.
 (8) Neuworth, K. B., Hofmann, Vera, Kelly, T. E., Ind. Eng. Chem. 43, 1689-94 (1951).